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VAPORIZATION THERMODYNAMICS IN THE VANADIUM-RICH
PORTION OF THE VANADIUM- (U) STATE UNIV OF NEW YORK AT
BINGHAMTON DEPT OF CHEMISTRY C E MYERS ET AL

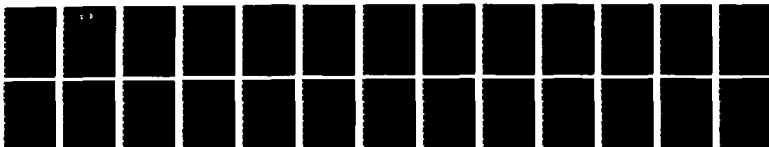
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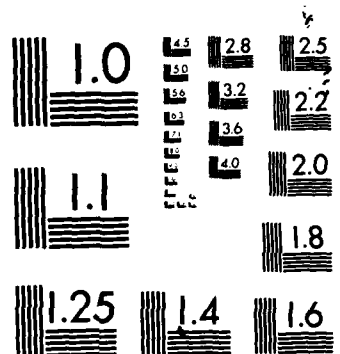
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Vaporization Thermodynamics in the Vanadium-Rich Portion
of the Vanadium-Silicon System
by High Temperature Knudsen Cell Mass Spectrometry

by

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VAPORIZATION THERMODYNAMICS IN THE VANADIUM-RICH PORTION
OF THE VANADIUM-SILICON SYSTEM
BY HIGH TEMPERATURE KNUDSEN CELL MASS SPECTROMETRY

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(Supported in part by the U. S. Office of Naval Research)

ABSTRACT

Vaporization behavior and phase equilibria in the vanadium-rich portion of the vanadium-silicon system ~~have been~~ ^{were} investigated by high temperature Knudsen cell mass spectrometry. At about 1900K and below the $V_3^{\text{n}}\text{Si}$ single-phase region was found to include congruently vaporizing compositions, and at about 2000K and above $V_5^{\text{n}}\text{Si}_3^{\text{n}}$ was found to be congruently vaporizing. In an intermediate temperature range both the $V_3^{\text{n}}\text{Si}$ and $V_5^{\text{n}}\text{Si}_3^{\text{n}}$ regions will contain congruently vaporizing compositions, and there will exist a local maximum in the total vapor pressure in the solid two-phase region; the term eutatmotic point is suggested for this maximum. The $V_3^{\text{n}}\text{Si}$ single-phase region was found to extend from 17.5 to 25.5 atomic percent silicon at 1800K. Thermodynamic activities leading to free energies of phase formation were measured by direct comparison with the solid elements. Enthalpies of phase formation at 298.15K, calculated from the experimental data in combination with published heat capacity and entropy data, are:

$1/4 V_3^{\text{n}}\text{Si}$, -5.37 kK; $1/8 V_5^{\text{n}}\text{Si}_3^{\text{n}}$, -6.33 kK.



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INTRODUCTION

The vanadium silicides are of interest as corrosion resistant materials and for their potential applications in the electronics industry. In addition, their cohesive energies may be used, together with those of other silicides and related compounds, to assess factors affecting the strengths of chemical bonds in these compounds. The compounds in the V-Si system (1) are V_3Si , V_5Si_3 , V_6Si_5 , and VSi_2 . Of these, only V_3Si has any significant range of homogeneity; V_6Si_5 is only stable above about 1160K (2). Several authors (1,3,4,5) have reviewed critically the published thermochemical data for the system. These reviews do not include a recent study (2) which employed Knudsen cell-mass spectrometry to obtain thermodynamic activities relative to the pure solid elements as a function of composition. The relative magnitudes of V and Si partial pressures at 1650K, as calculated from these experimental activities and published sublimation pressure data for the pure elements, suggested that V_5Si_3 vaporizes congruently (i.e. vapor and condensed phase have the same composition) at this temperature. However, the possibility could not be ruled out that the V_3Si region contains the congruently vaporizing composition. The goals of the present work were to determine which phase region contains the congruently vaporizing composition, to obtain more precise measurements of thermodynamic activities in the metal-rich portion of the system, and to examine in more detail the homogeneity range of V_3Si . Activities as a function of composition and temperature were determined relative to the pure solid elements by means of a high temperature mass spectrometer. Owing to uncertainties in partial pressures, derived from uncertainties in activity measurements and in reported sublimation pressures on the pure elements, calculation of congruently vaporizing

compositions from these data are not unambiguous. Hence studies of compositional changes upon vaporization were undertaken.

EXPERIMENTAL

Vanadium silicide samples were prepared by arc melting weighed mixtures of elemental vanadium and silicon under an argon atmosphere. Many samples shattered upon cooling which made estimation of weight loss difficult. Other samples were observed to lose as much as 2% of their total weight during melting.

Phase analysis was performed by Debye-Scherrer X-ray powder diffraction. Observed powder patterns were compared with patterns calculated by computer from published structural data. Diffraction patterns were taken of both as cast samples and residues from various extended heating and mass spectrometer experiments.

Selected residues were analyzed by wet chemical techniques. Vanadium content was established by titration with ferrous ammonium sulfate (6) after decomposing the sample with fused NaOH (7), dissolving in dilute HCl, and adjusting the oxidation state to +5 with permanganate. The vanadium determinations were reproducible to $\pm 0.5\%$.

Thermodynamic activities of vanadium and silicon were determined by means of the high temperature mass spectrometric method (2). The equipment used was a 90° sector, single focusing, high resolution magnetic deflection instrument manufactured by Nuclide Corporation. A block diagram of the data acquisition and control system is given in Figure 1. The sample was placed in a tungsten metal cup within a tungsten metal effusion cell which was heated by radiation from a tungsten helix resistance heating element. The entire furnace assembly was surrounded by tungsten and tantalum radiation shields within a water

cooled vacuum enclosure. Temperatures were measured with a tungsten-rhenium thermocouple inserted into the base of the effusion cell; the thermocouple was calibrated by means of an optical pyrometer sighted through the orifice into the interior of the effusion cell. The design of the mass spectrometer was such that the molecular beam from the effusion cell, the path of the ionizing electrons, and the ion beam were all mutually perpendicular. Silicon signals were obtained with ionizing electron energies of 12.5 eV in order to minimize the effects of the mass 28 background. The resolution of the instrument was such that, at this electron energy, the silicon peak at mass 28 was effectively separated from the carbon monoxide/nitrogen peak as shown in Figure 2. An ionizing energy of 30.0 eV was used for the vanadium data. Ion currents as a function of temperature were obtained for both V, mass 51, and Si, mass 28, from 10 to 37 atom percent silicon. Immediately before or after measuring the V or Si ion intensities over a vanadium silicide sample, a sample of elemental V or Si was placed in the Knudsen cell, and ion intensities were recorded as a function of temperature. Thermodynamic activities were calculated by comparison to the elements as described below. It should be noted that the same Knudsen cell was used in experiments for both the silicides and the elements, but different tungsten cups were used for the respective V, Si or V-Si samples.

In the experiments for determination of compositional changes upon vaporization, samples were heated in vacuum for extended periods with the crucible lid removed and were analyzed for vanadium before and after heating. The duration of these experiments ranged from 12 hours at 2100K to 120 hours at 1900K.

THERMODYNAMIC CALCULATIONS

Thermodynamic activities relative to the pure solid elements were obtained as follows. The partial pressure of a species in a Knudsen cell-mass spectrometry experiment is proportional to IT , where I is the ion current due to that species and T is the temperature of the effusing vapor. Hence the thermodynamic activity of a species in the sample is given by $a = I/I^\circ$, where I is measured for the element above the sample and I° is measured above the pure element under the same experimental conditions of temperature, orifice area, and electron energy (2). Although I and I° are measured in different experiments, the mass spectrometer is sufficiently stable that reproducible results are obtained. In practice, activities at a given temperature were calculated from slopes and intercepts of $\log IT$ and $\log I^\circ T$ vs $1/T$ plots:

$$\log a_i = (A_i - A_i^\circ)/T + (B_i - B_i^\circ) \quad (1)$$

where A_i and A_i° are the slopes and B_i and B_i° are the intercepts of $\log IT$ vs $1/T$ plots for the sample and pure element respectively.

The activities evaluated at 1650K were used to calculate the free energies of formation of V_3Si and V_5Si_3 :



$$\Delta G_f^\circ/R = 2.303 T \log a_V^{(1-x)} a_{Si}^x \quad (3)$$

where x is the atom fraction of Si in the respective solid. The geometric mean (average of $\log a$) was used for the vanadium activity in the V_5Si_3 - V_3Si two-phase region. Entropy and heat capacity data for the silicides cited or estimated by Smith (1) were used, together with

Smith's data (8) for V and data from the JANAF Tables (9), to calculate $\Delta H_f^\circ, 298.15/R$ from the free energy of formation data at 1650K.

RESULTS

Scans with the mass spectrometer established that, at the level of detectability of the instrument, there were no gaseous vanadium-silicon species in the temperature range of the experiments. Typical data are shown in Figure 3. The experimentally determined activity parameters are given in Table 1 and activities as a function of composition at 1650K and 1800K are shown in Figure 4. In the present work the vanadium activity in the V_5Si_3 - V_3Si two-phase region was found to be somewhat greater than was observed by Storms and Myers (2). In addition, the variation of the logarithm of the vanadium activity with atom fraction silicon across the V_3Si single-phase region was found to be approximately linear; this permits a much more precise and unambiguous determination of the homogeneity range which was found to extend from 17.5 to 25.5 atom percent silicon at 1800K as shown in Figure 4b. Thermodynamic stability data calculated from the experimental results are given in Table 2. Agreement with the data from the earlier mass spectrometric study (2) is quite good.

The results of the extended heating experiments are shown in Figure 5. The arrows give the direction and extent of composition change during heating; the figures over the arrow are the mass loss and the initial sample mass in milligrams. The temperature uncertainty is ± 10 -20K. Compositions of samples heated at about 1900K and below move past V_5Si_3 toward the V_3Si single-phase region. Above 2000K, compositions move through the V_3Si single-phase region toward V_5Si_3 .

DISCUSSION

Vaporization behavior in the vanadium-rich portion of the V-Si system may be understood in terms of the schematic pressure vs composition diagrams shown in Figure 6. The use of P-X diagrams to interpret vaporization behavior has been discussed by Gilles (10) among others. We conclude that at 1900K and below congruently vaporizing compositions (the specific composition will depend on temperature) will be found within the V_3Si single-phase region as shown in Figure 6a. This conclusion is based on the considerations: a) the composition of a sample richer in silicon than V_5Si_3 moves past that composition toward V_3Si upon extended vaporization, and b) partial pressure ratios (P_{Si}/P_V), calculated from the thermodynamic activity for compositions more vanadium-rich than the V_3Si single-phase region, are orders of magnitude too low for congruent vaporization to occur in this composition range. We term this congruent vaporization convergent since the composition will move toward the congruently vaporizing composition upon vaporizing samples of either higher or lower silicon content. For temperatures at or above 2000K we conclude that V_5Si_3 will be congruently vaporizing (and convergent) as shown in Figure 6c. This conclusion is based on the considerations: a) samples richer in vanadium than the V_3Si single-phase region move through that region toward V_5Si_3 upon extended vaporization, and b) calculated partial pressure ratios (P_{Si}/P_V) for samples more silicon-rich than V_5Si_3 are orders of magnitude too high for congruent vaporization to occur. The upper temperature limit of these calculations is the incongruent melting temperature of V_6Si_5 at about 1950K (1). This limit also precluded extended vaporization studies above 1950K on samples more rich in silicon than V_5Si_3 since molten samples attack the tungsten containers.

As temperature is raised from 1900K to 2000K there must be a continuous transition from the situation described by Figure 6a to that described by Figure 6c. As a consequence, there must be an intermediate range of temperatures for which Figure 6b applies. In this range both V_3Si and V_5Si_3 contain convergent congruently vaporizing compositions, and there will be a series (with compositions depending on temperature) of local maxima in the total vapor pressure which are congruently vaporizing in the divergent sense. We propose the term euatmotic (Gk. easy vaporizing) for such a local maximum, in parallel with the more familiar term eutectic (Gk. easy melting).

The vaporization characteristics of the V-Si system (at 2000K) are summarized in Figure 7. The two curves in this figure both plot the X_{Si}/X_V ratio in the gas phase vs the X_{Si}/X_V ratio in the condensed phase. Curve I (the "stair step" curve) may be described by the relation

$$X_{Si}^g/X_V^g = P_{Si}/P_V = (a_{Si}P_{Si}^0)/(a_V P_V^0) \quad (4)$$

where experimentally measured a_{Si} and a_V data and literature P_{Si}^0 and P_V^0 data have been used to calculate the values plotted in the various regions. Curve II is described by

$$X_{Si}^g/X_V^g = P_{Si}/P_V = (X_{Si}^s/X_V^s)(M_{Si}/M_V)^{1/2} \quad (5)$$

which is the relation that must be obeyed if a sample of composition X_{Si}^s is to vaporize congruently under Knudsen conditions. Compositions at which the two plots cross are congruently vaporizing. If Si/V for the vapor is constant (two solid phases) the intersection is the euatmotic composition, whereas if Si/V for the vapor is not constant (one solid phase) the intersection represents a convergent congruently vaporizing

composition. While the existence of a single convergent congruently vaporizing composition is common, systems with two such compositions are relatively rare; known examples include some of the rare earth metal-sulfur systems (11,12).

The existence of a congruently vaporizing composition within a metal-silicon system depends upon a rough matching of the volatilities, and hence of sublimation enthalpies, of the metal and silicon. In systems for which the metal has a very low sublimation pressure (such as Ta-Si (13)) silicon will be lost preferentially at all compositions. On the other hand, if the metal is much more volatile than silicon (as in the Mn-Si system (14)), it will be lost preferentially at all compositions. The location of the congruently vaporizing composition within the particular metal-silicon system also depends upon relative volatilities. Since vanadium is less volatile than silicon, the congruently vaporizing compositions in the V-Si system appear in the vanadium-rich portion. However, in the Cr-Si system (15), the congruently vaporizing composition is in the CrSi_2 single phase region since chromium is more volatile than silicon.

ACKNOWLEDGEMENTS

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RUNNING TITLE: Vaporization of Vanadium Silicides

INDEX ENTRIES: Vanadium silicides, V_3Si , V_5Si_3 , range of homogeneity, vaporization behavior, congruent vaporization, euatmotic point, thermodynamic activities, free energy of formation, enthalpy of formation.

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TABLE 1

ACTIVITY PARAMETERS FOR VANADIUM-SILICON SYSTEM

X(Si)	A(V)	A°(V)	B(V)	B°(V)	T Range(K)	Log a(V)	
						1650K	1800K
0.3187	-27270	-26490	9.008	9.087	1737-1984	-0.552	-0.512
0.2206	-25770	-25800	8.293	8.626	1811-2002	-0.315	-0.316
0.3655	-26750	-25700	7.625	7.531	1846-2063	-0.542	-0.489
0.3093	-28210	-26870	8.921	8.663	1788-2054	-0.554	-0.486
0.2426	-27050	-26510	8.746	8.877	1734-1937	-0.458	-0.431
0.1998	-25750	-25590	7.647	7.755	1765-2041	-0.205	-0.197
0.2132	-26710	-25590	8.095	7.755	1748-2039	-0.339	-0.282
0.2439	-27530	-25590	8.406	7.755	1743-2036	-0.525	-0.427
0.1968	-25480	-25590	7.523	7.755	1701-1995	-0.165	-0.171
0.1054	-25470	-25590	7.644	7.755	1717-2012	-0.038	-0.044
0.1693	-24420	-25590	7.054	7.755	1709-2003	0.008	-0.051

X(Si)	A(Si)	A°(Si)	B(Si)	B°(Si)	T Range(K)	Log a(Si)	
						1650K	1800K
0.3187	-26490	-22100	7.909	8.177	1797-1997	-2.929	-2.707
0.2206	-29370	-21160	8.942	7.177	1785-2029	-3.211	-2.796
0.2426	-28790	-23590	8.955	9.139	1696-1940	-3.336	-3.073

TABLE 2

THERMODYNAMIC DATA FOR VANADIUM SILICIDES

- $\Delta G_f^0, 1650K/R$ (kK)		Source
1/4 V_3Si	3.63	Si and V activities (22 a/o Si)
	4.39	Si and V activities (24 a/o Si)
	4.35	Si and V activities, $V_5Si_3 + V_3Si$ (32 a/o Si)
	4.40	Storms and Myers (2), $V_5Si_3 + V_3Si$
1/8 V_5Si_3	5.49	Si and V activities, $V_5Si_3 + V_3Si$ (32 a/o Si)
	5.47	Storms and Myers (2), $V_5Si_3 + V_3Si$
- $\Delta H_f^0, 298.15/R$ (kK)		
1/4 V_3Si	5.39	Si and V activities (24 a/o Si)
	5.35	Si and V activities, $V_5Si_3 + V_3Si$
	5.40	Storms and Myers (2), $V_5Si_3 + V_3Si$
	5.18	Smith (1)
1/8 V_5Si_3	6.33	Si and V activities, $V_5Si_3 + V_3Si$
	6.31	Storms and Myers (2), $V_5Si_3 + V_3Si$
	6.47	Smith (1)

FIGURE CAPTIONS

1. Data acquisition and control system.
2. Instrument resolution and electron energy at mass 28.
3. Typical data: Log IT vs $1/T$ for sample and solid element standards.
4. Log activity vs composition: (a) 1650K, (b) 1800K. Squares, this work; circles, Reference 2.
5. Extended heating experiments: Arrows indicate direction and extent of composition change; in figures over each arrow, numerator is mass loss (mg) and denominator is initial mass of sample.
6. Pressure vs composition (schematic).
7. Gas phase composition ratio, X_{Si}/X_V , at 2000K:
I. Observed; II. Calculated for congruent vaporization under effusion conditions.

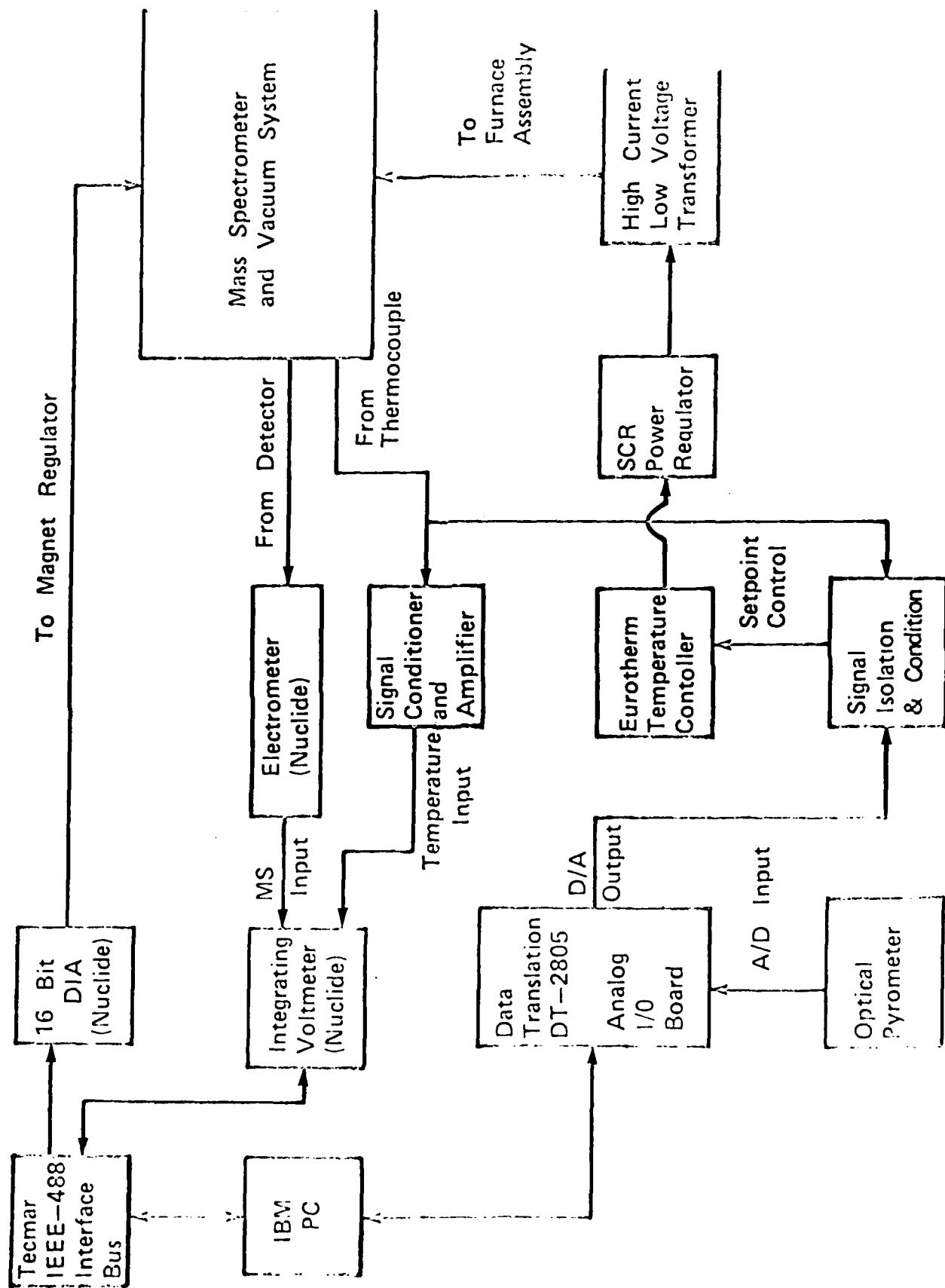


Figure 1

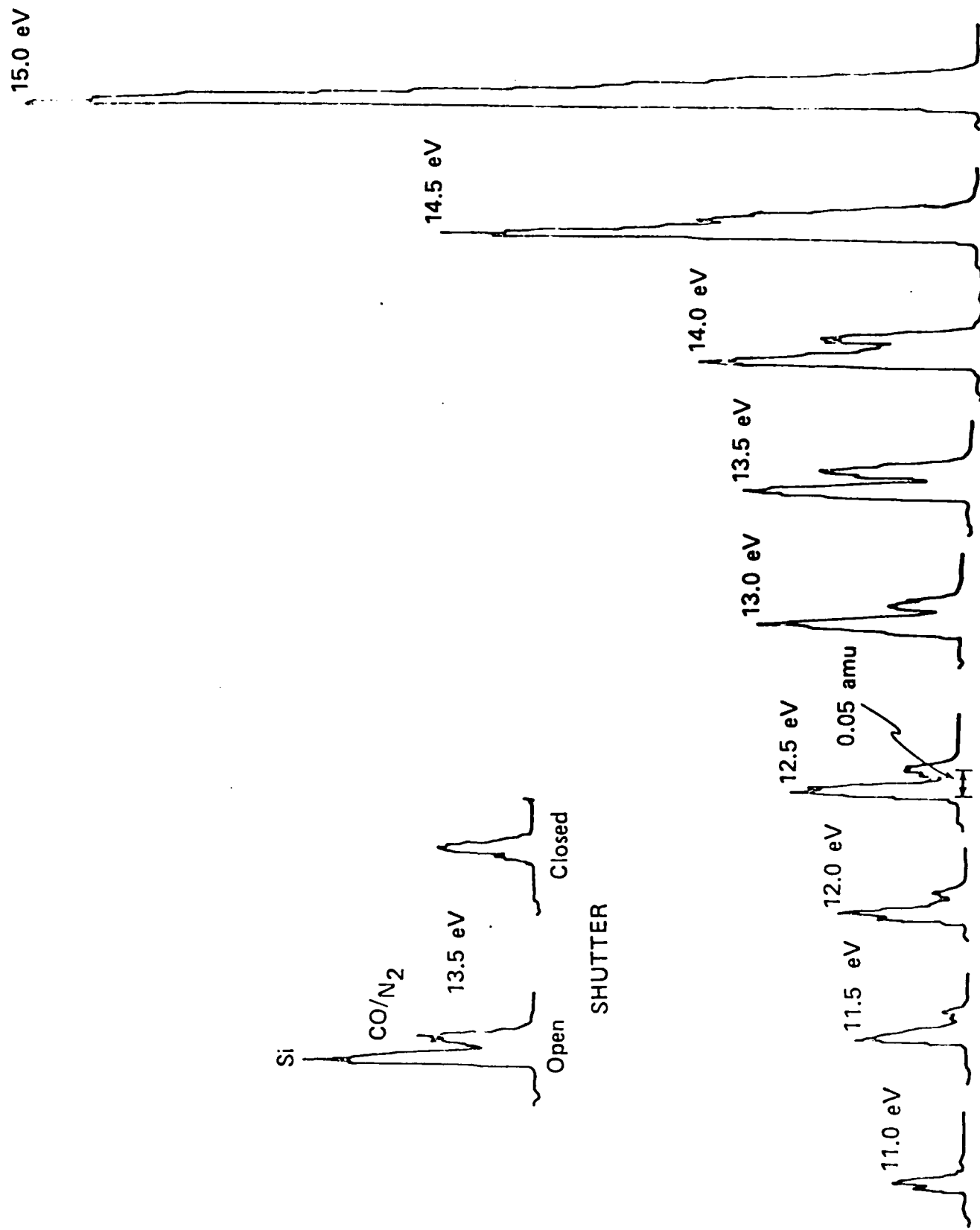


Figure 2

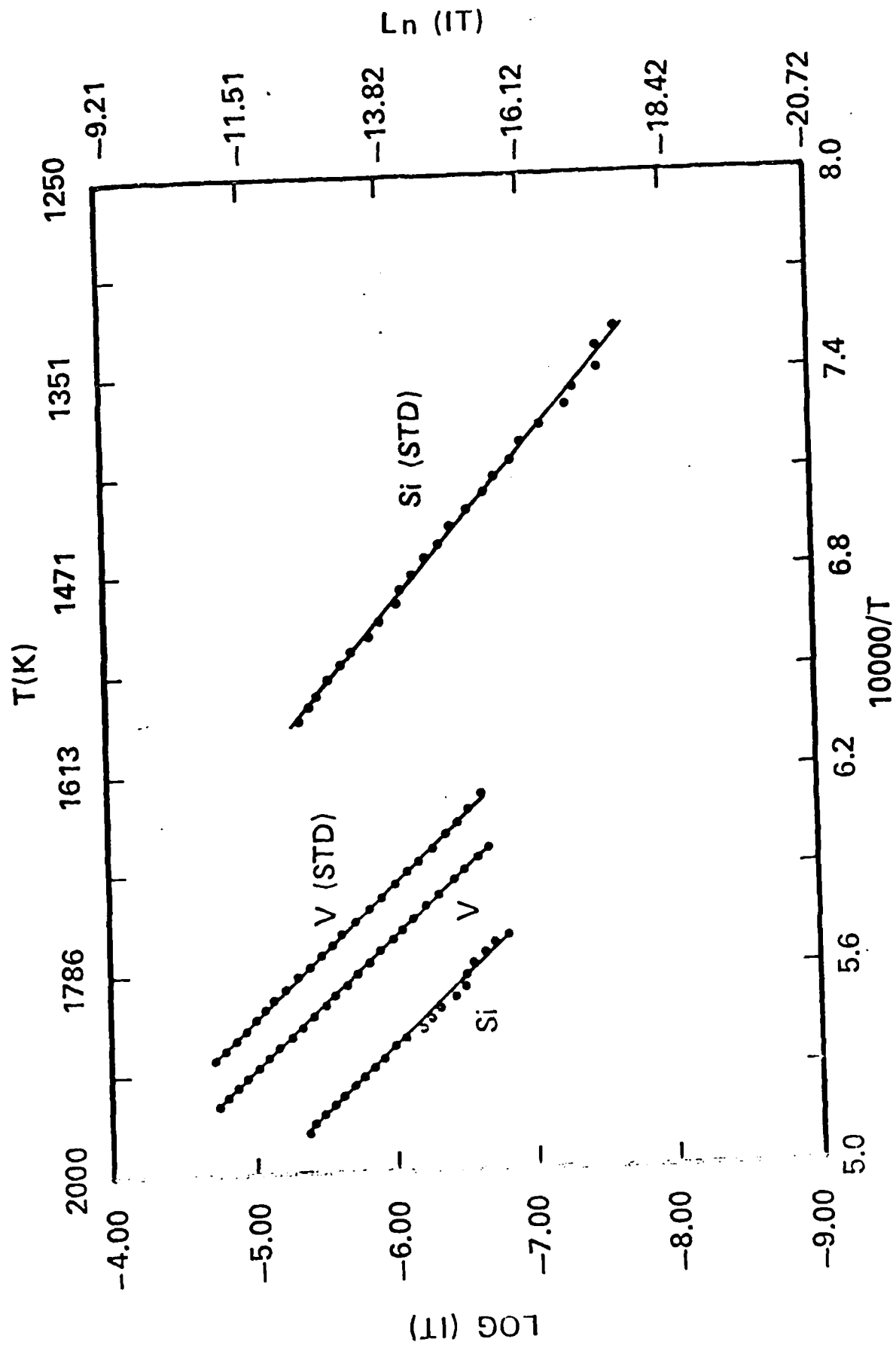


Figure 3

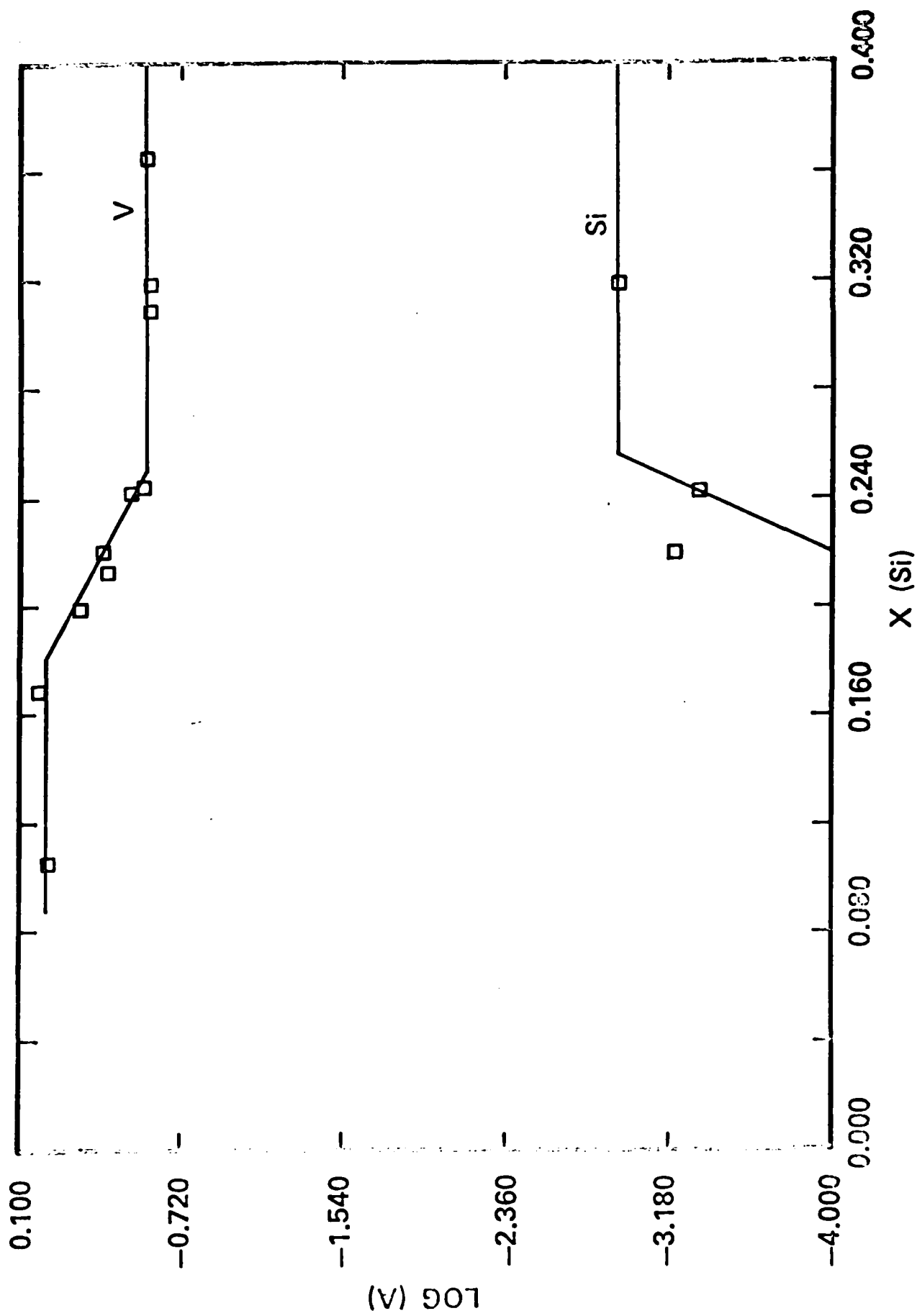


Figure 4a

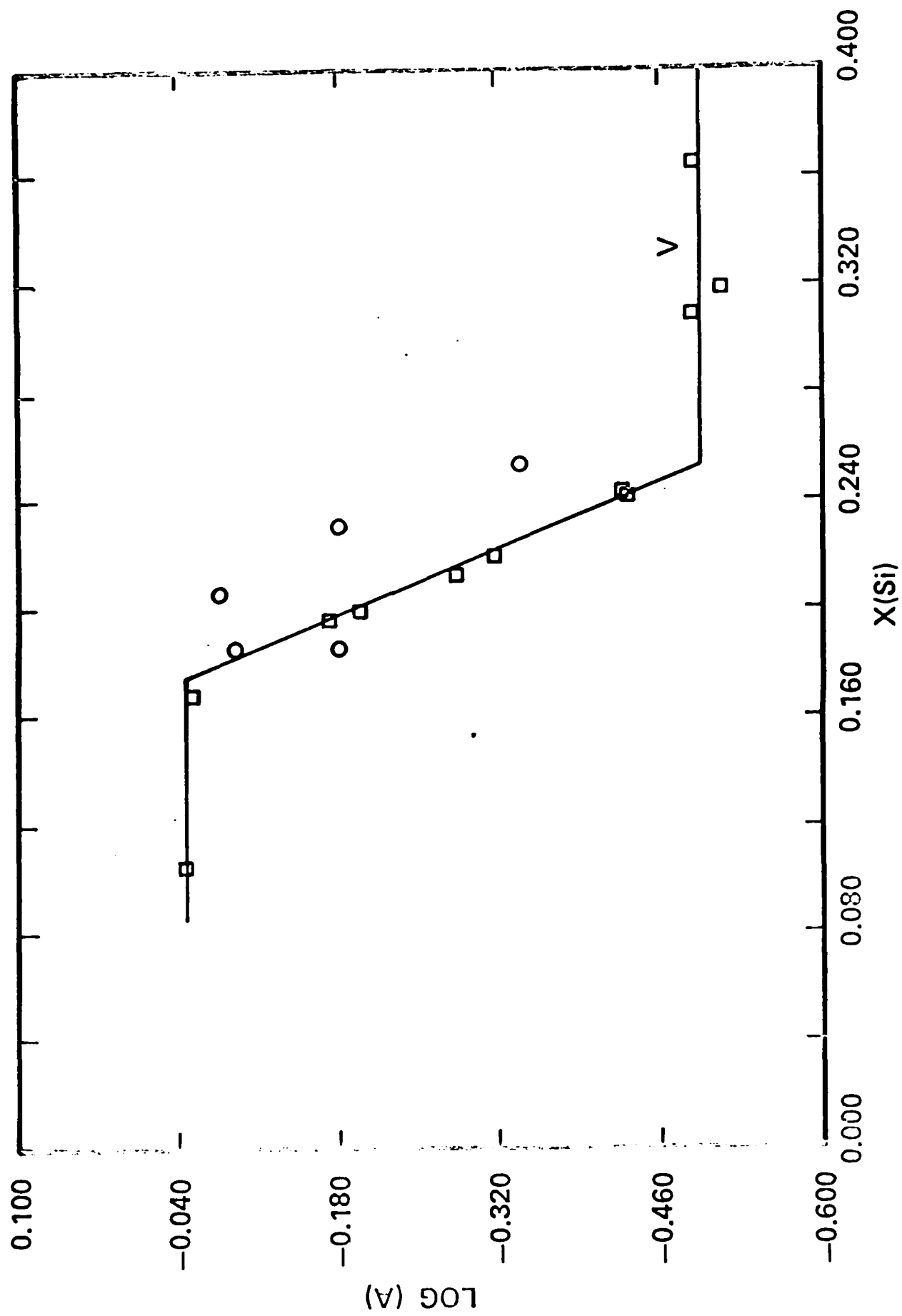
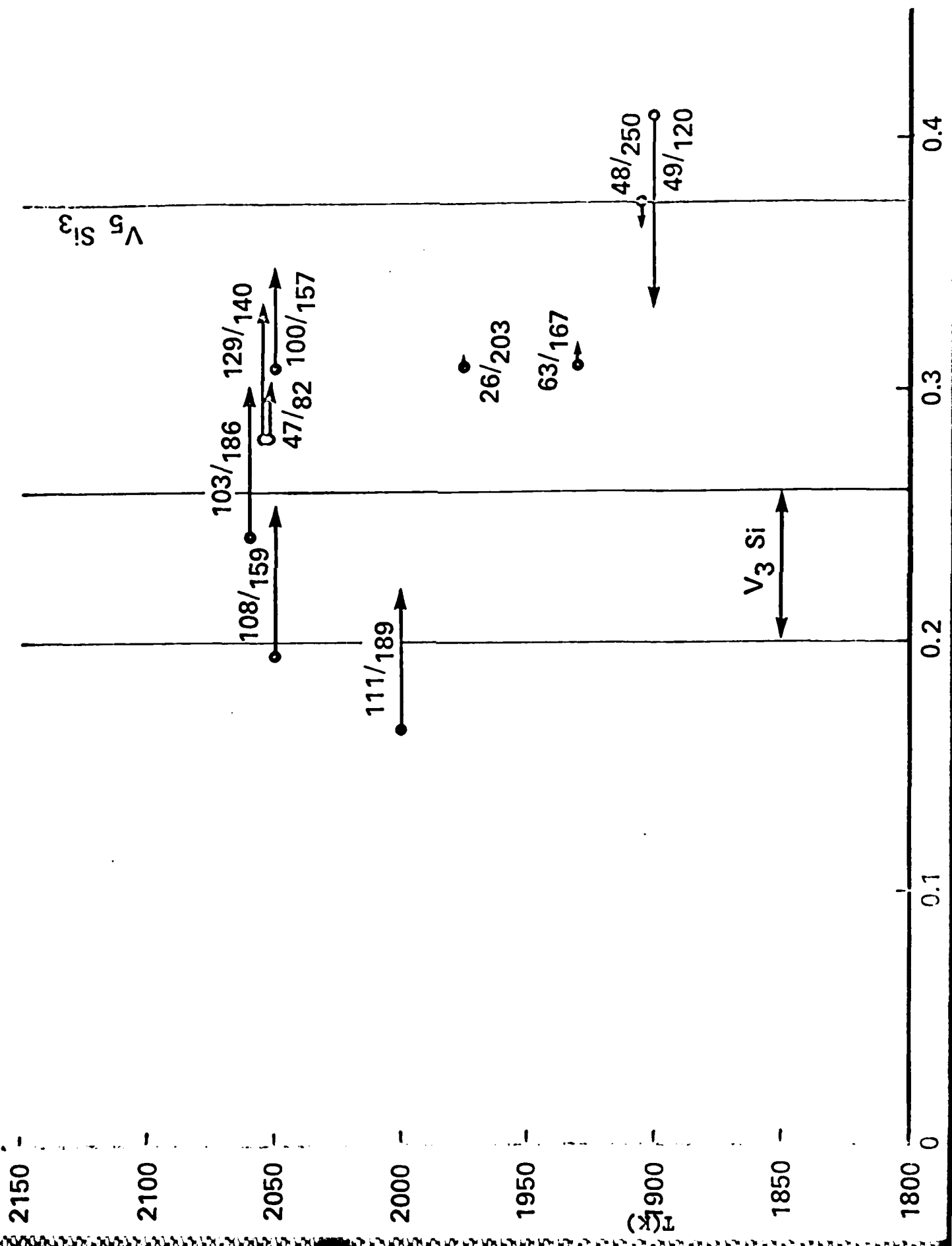


Figure 4b



(a) V_3Si Congruent ($T \leq 1900K$)

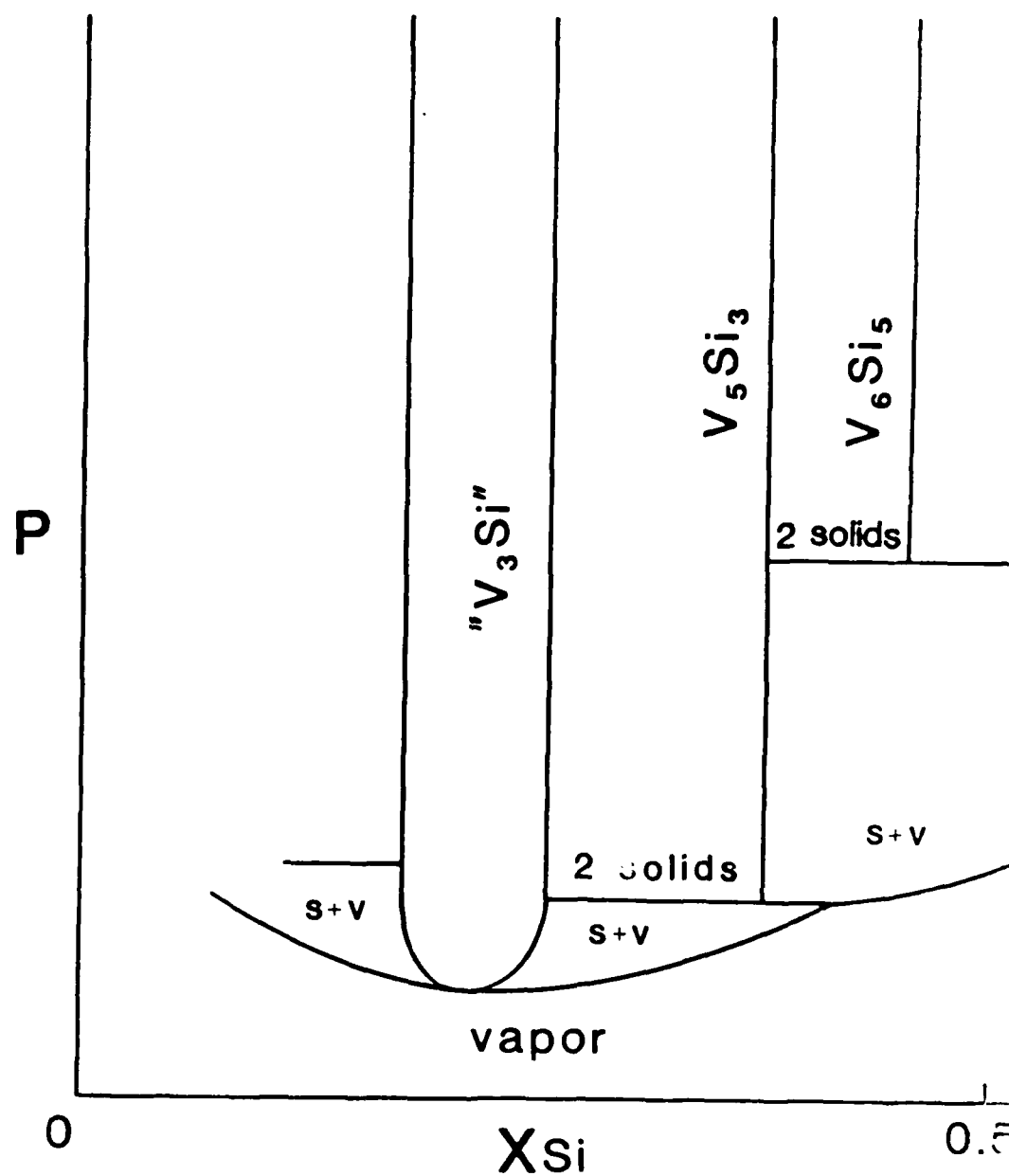


Figure 6a

(b) Both V_3Si and V_5Si_3 Congruent
 ($1900K < T < 2000K$)

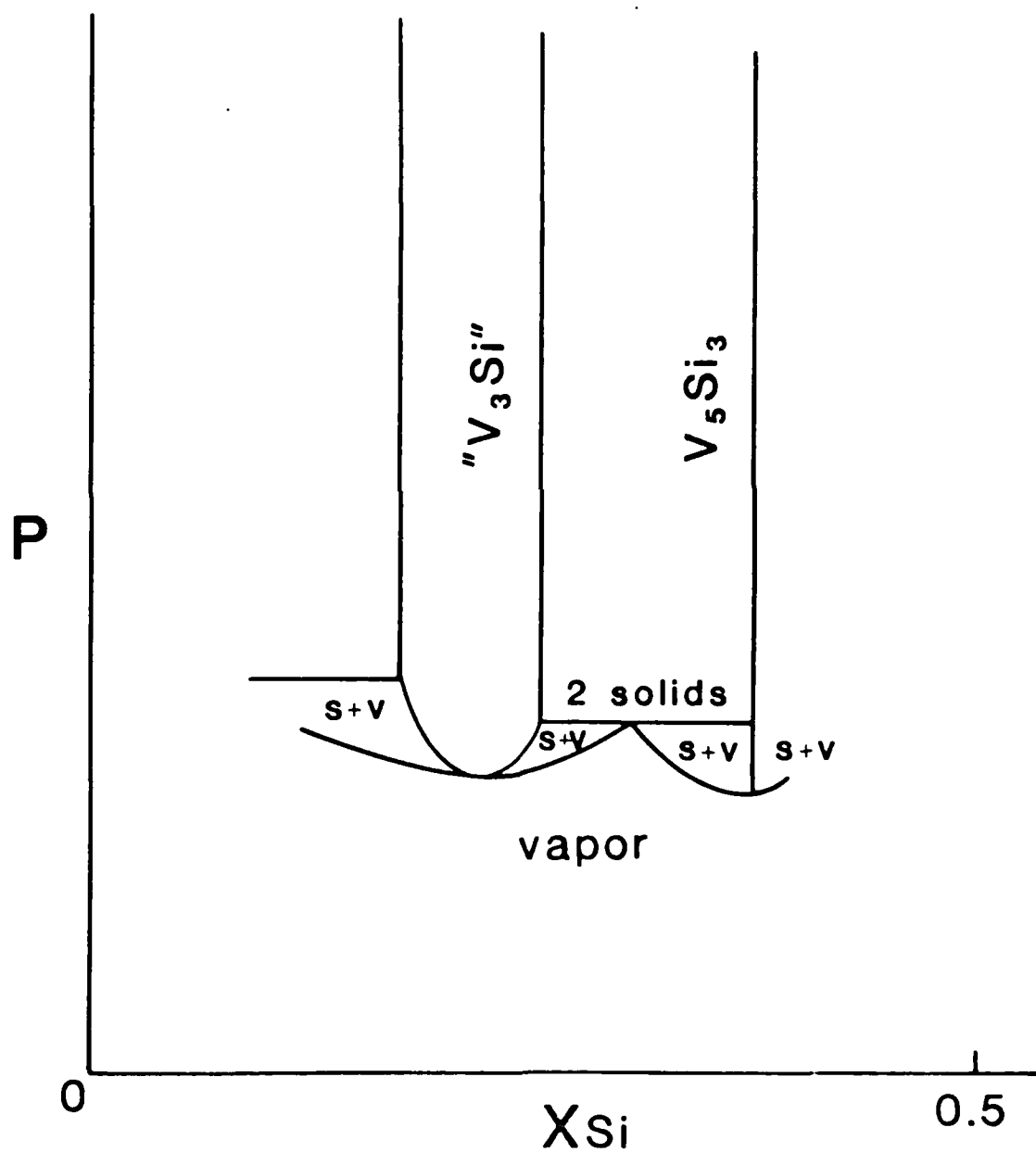


Figure 6b

(c) V_5Si_3 Congruent (T ≥ 2000 K)

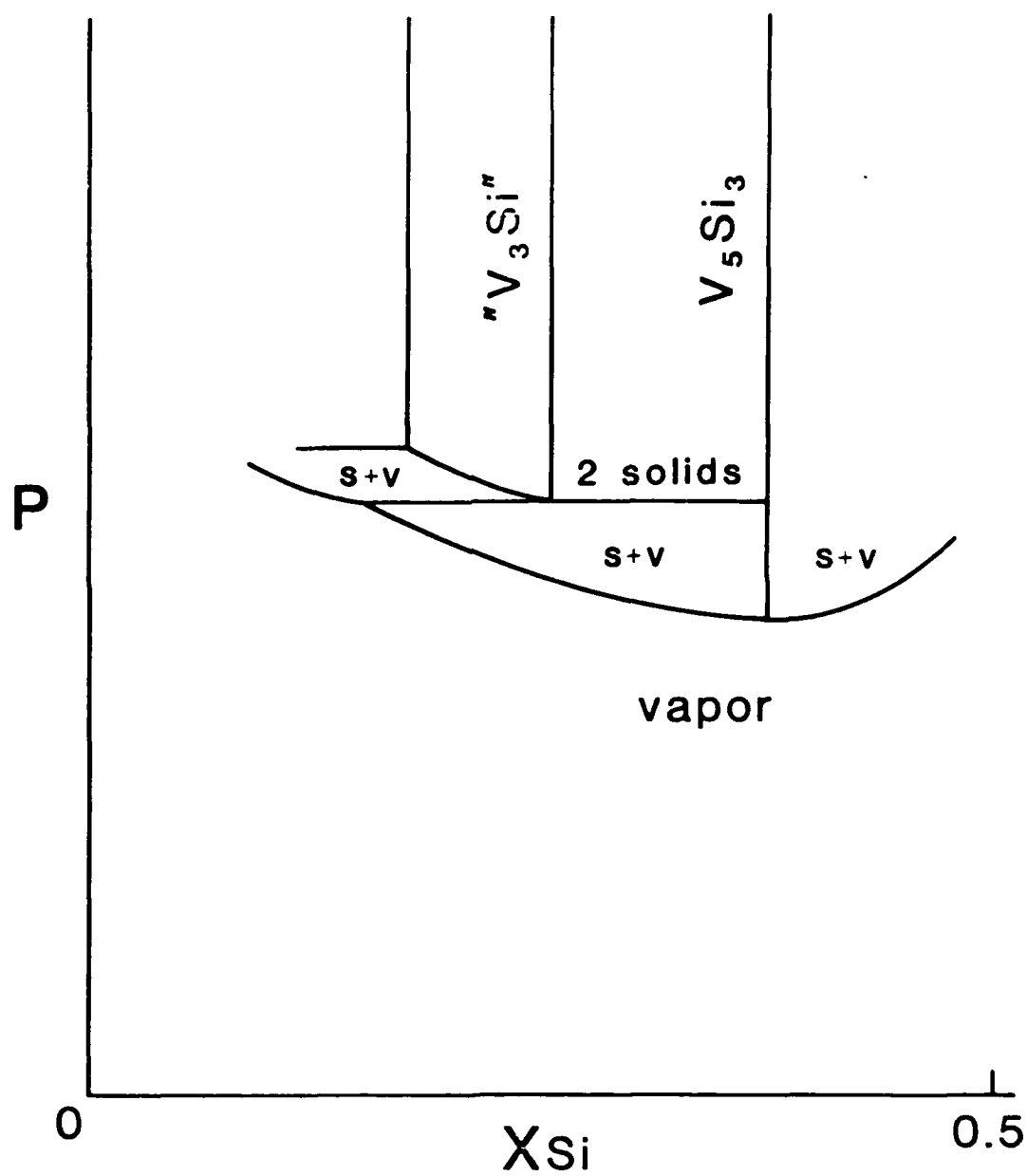


Figure 6c

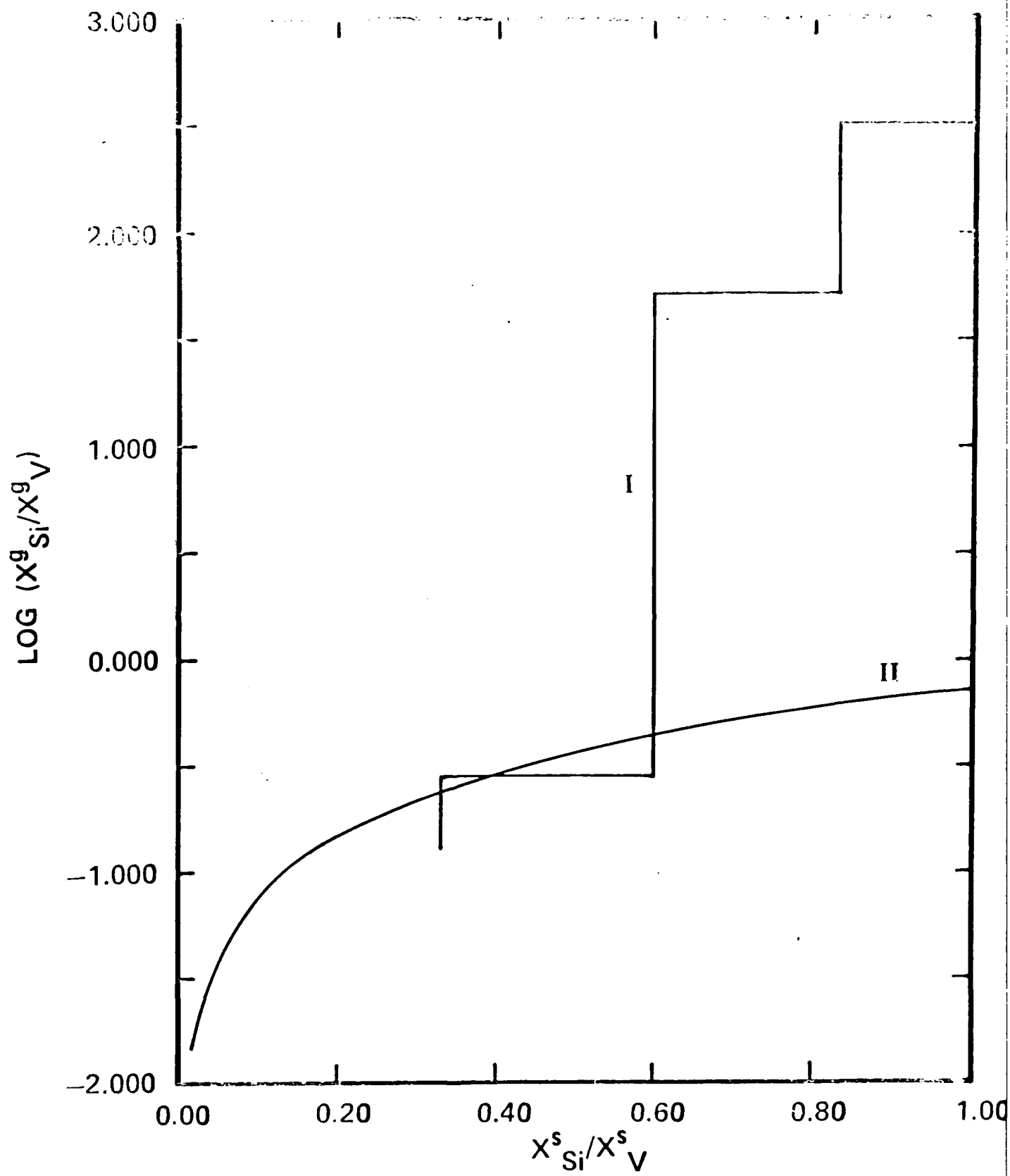


Figure 7

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